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CERAMIC CLAYS FROM VORONEZH OBLAST

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The Latnensk deposit of refractory clays and the Shramovsk deposit of refractory clays suitable for production of ceramics ware are examined.

The demand for clay raw materials for production of high-quality ceramic facing articles has increased in recent years due to the increase in major construction. Voronezh Mine Management Co. is developing the Latnensk deposit of refractory clays which are widely used in production of different ceramic and porcelain-faience ware. In addition, a new deposit of refractory clays suitable for use in the ceramics industry has been discovered in the southern part of Voronezh oblast.

The **Latnensk refractory clay deposit** is located 15 km west of Voronezh. It has been known since the last century. Development of the deposit by inefficient quarries began in the second half of the 19th century, and industrial development began in 1900. The clays were initially primarily used for production of ceramics, and in the Soviet period, for manufacturing refractory ware. Voronezh Mine Management Co. is now working the deposit. Three quarries are operating: "Srednii," "Belyi Kolodets," and "Strelitsa Blizhnyaya."

The basic mineral resources are kaolin clays confined to chalky deposits of the Aptian. The deposits usually have the form of round-elongated lenses from hundreds of meters to several kilometers wide. The absolute roof markers vary from 122 – 130 to 104 – 112 m. The thickness of the clays varies from 0.5 to 16.5 m and is 3 – 4 m on average. The clays are usually light gray and gray, changing to black in places as a function of the organic inclusion content. Pyrite and marcasite concretions whose content increases in carbonified varieties are observed in places. The clay in the upper parts of the cuts can acquire spotty brownish-red coloring caused by oxidation of iron-containing minerals and the appearance of trivalent iron oxides.

The productive series is of complex structure and the quality of the clays is inconsistent both in extent and in depth. A common characteristic is observed: sandy clays usually lie in the lower part of the deposit, while finely disperse clays are in the middle, and carbonaceous varieties complete the section. Five lithological varieties of clays have been distinguished: gray plastic (0.05 – 2.1 m), sometimes sandy ferruginous; dark gray plastic (0.1 – 1.6 m), less frequently sandy; light gray, primarily sandy (0.25 – 2.7 m), less frequently plastic; black fat, plastic (0.1 – 1.6 m), frequently oversanded and ferruginous; variegated, ranging from light yellow to brown (0.1 – 0.7 m), strongly ferruginous sandy.

The clays occur in sandy-gravel rocks from the Aptian with a depth of 1 to 40 m and are valuable mineral resources which are worked in association and used in construction, for manufacturing abrasives, etc. Refractory clays with Cretaceous Neogenic formations with a total depth of 0 to 70.0 m overlap. The overlapping rocks are composed of quartz sands

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TABLE 1

Clay	Average content, %										
	SiO_2	SiO_2 (free)	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	calcination loss
LOC	54.50	6.00	40.20	2.00	1.10	0.75	0.15	0.16	0.30	0.08	14.30
LT1	56.70	7.00	38.40	2.00	1.20	0.70	1.15	0.20	0.30	0.10	12.70
LT2	60.70	8.80	35.50	2.05	1.05	0.70	0.60	0.10	0.30	0.10	11.50
LT3	64.50	21.80	31.20	1.90	1.15	0.60	0.60	0.10	0.40	0.15	10.70
LTPK	68.70	32.10	26.35	1.70	1.05	0.40	0.30	0.10	0.45	0.15	9.50
LTK	79.90	37.00	16.00	1.30	1.45	0.20	0.60	0.15	0.25	0.05	6.50
LTU	64.80	20.10	29.70	1.50	1.20	1.10	1.90	0.10	0.40	0.80	24.10

TABLE 2

Clay	Mass content, %, fraction, mm							Dispersion	Plasticity number
	> 0.5	0.5 – 0.25	0.25 – 0.063	0.063 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001		
				Strelitsa Blizhnyaya Section					
LOC	0.20	0.42	0.58	11.32	5.28	13.16	69.04	High	22.61
LT1	0.10	0.34	0.76	8.96	3.92	14.04	71.88	″	22.22
LT2	0.10	0.20	0.70	27.52	4.92	12.80	53.76	Medium	14.17
LT3	0.20	0.30	4.50	11.96	7.64	12.44	62.96	High	Not determined
LTPK	0.26	0.18	0.92	42.28	4.08	16.28	36.00	Low	12.59
				Belyi Kolodets Section					
LOC	0.02	0.20	0.38	3.68	2.80	21.00	71.92	High	21.86
LT1	0.02	0.18	0.30	4.66	3.64	13.20	78.00	″	Not determined
LT2	0.20	0.40	1.60	18.76	4.52	12.08	62.44	″	22.94
LT3	0.11	0.22	1.97	23.34	8.92	17.28	48.16	Medium	14.60
LTPK	0.14	0.10	1.54	37.26	8.96	17.76	34.24	Low	12.46
LTK	3.10	3.00	16.90	24.80	2.60	15.28	34.32	″	9.45
LTU	1.04	0.20	0.56	18.92	8.36	28.08	42.84	Medium	15.44
				Srednii Section					
LT1	0.08	0.20	0.84	3.24	3.00	6.84	85.80	High	27.49
LT2	0.40	1.60	1.50	3.54	5.52	15.00	72.44	″	18.08
LT3	0.32	0.40	10.00	26.04	4.40	13.56	45.28	Medium	14.60
LTPK	0.13	0.80	20.47	32.76	4.92	12.64	28.28	″	13.08

of different size, nodular phosphorites, chalks, clays, and loams.

The clays in the Latnensk deposit are clear-firing. With respect to refractoriness, they belong to the refractories group. The refractoriness varies from 1730 to 1670°C. Based on the alumina content, the clays are subdivided into highly basic, basic, and semiacid. One variety of highly basic clays LOC (special) with an Al_2O_3 content above 39% and three varieties of basic clays (LT1, LT2, LT3) with an Al_2O_3 content from 28 to 39% and two varieties of semiacid clays with an Al_2O_3 content from 23 to 28% (LTPK) and from 15 to 23% (LTK) are distinguished. Carbonaceous clays (LTU) are also distinguished. The chemical composition of the Latnensk clays is reported in Table 1.

TABLE 3

Clay	Mass content, %			
	kaolinite	montomorillonite	gibbsite	hydromica
		Strelitsa Blizhnyaya Section		
LOC	80	20	–	–
LT1	75	20	5	–
LT2	70	20	10	–
LT3	80	20	–	–
LTPK	90	10	–	Traces
		Belyi Kolodets Section		
LOC	80	15	5	–
LT1	70	20	10	–
LT2	85	15	–	–
LT3	85	10	5	Traces
LTPK	90	10	–	″
LTK	90	10	–	″
		Srednii Section		
LT2	95	Traces	5	Traces
LT3	90	10	–	–
LTPK	90	10	–	–

The clays basically belong to the group with average coloring oxide content. The mass fraction of Fe_2O_3 varies from 0.70 to 1.73% and sometimes rises to 2.50%; TiO_2 varies from 0.93 to 1.92% and rarely goes up to 2.45%.

In LOC and LT1 clays, the free silica content is low (4.80 – 7.25%), average in LT2, LT3, and carbonaceous clays (11.85 – 22.65%), and average and high in semiacid clays (23.40 – 39.20%).

The basic varieties of the clays are highly disperse. The content of the less than 0.001 mm fraction varies from 62.44 to 85.80%, and semiacid average- and low-dispersion clays are characterized by a content of the less than 0.001 mm fraction from 53.76 to 28.28% (Table 2). They are primarily weakly oversanded (the total residue in a No. 063 sieve is 0.60 – 2.30% and increases to 23% in semiacid clays).

Kaolinite (75 – 95%) predominates in the mineral composition of the clays, and montomorillonite (0 – 20%) and hydromica are present in small amounts, while the nonargillaceous minerals are represented by quartz, gibbsite, iron hydroxides, sulfides, and carbonaceous matter (Table 3).

The detrital material in the clays is represented by quartz (85.8%) and feldspar (under 14.8%). Zirconium, rutile, disthene, staurolite, tourmaline, garnet, and ilmenite are observed in isolated grains.

The basic varieties of the clays usually belong to the group of raw materials with a low content of coarse-grained inclusions with predominance of small inclusions. In semiacid clays, the content of coarse-grained inclusions is

TABLE 4

Clay	Shrinkage		Water absorption, %	Density, g/cm^3
	air	total		
Strelitsa Blizhnyaya Section				
LOC	6.8	17.4	2.01	2.00
LT1	7.4	17.0	2.13	2.04
LT2	8.0	15.0	7.94	2.01
LT3	7.6	12.0	13.62	1.83
LTPK1	6.0	9.0	14.58	1.66
Belyi Kolodets Section				
LOC	8.2	19.6	2.17	2.12
LT1	9.6	20.4	2.15	2.19
LT2	7.4	14.4	8.15	1.93
LT3	7.0	11.6	12.60	1.77
LTPK1	6.6	10.0	12.50	1.77
LTPK2	5.8	7.2	14.75	1.61
Srednii Section				
LT1	9.8	20.8	0.58	2.08
LT2	7.8	17.0	7.22	2.15
LT3	6.4	10.0	14.39	1.76
LTPK1	5.6	7.6	13.09	1.72

low and average, with predominance of small and average. The inclusions are basically represented by quartz sand, crystalline rock fragments, and rarely iron hydroxides 0.5 – 7.0 mm in size.

The fundamental varieties of the clays are average-plastic and rarely moderately plastic. Semiacid clays are basically moderately plastic and carbonaceous clays are average-plastic.

Physicomechanical Properties of the Clays

Natural moisture content, %	22 – 26
Density, tons/m^3:	
specific	2.6
bulk	2.0
Porosity, %	37.9
Porosity coefficient	0.61
Internal friction angle, deg	13
Cohesion, MPa	0.038

LOC and LT1 clays from all sections have average sintering temperatures, with strong and medium sintering at 1250°C, water absorption of 0.58 – 3.91%, and total shrinkage of 17.0 – 20.8%. The sintered material is light beige with grey overtones and a smooth surface.

LT2 clays from the Srednii Section sinter at 1300°C and have water absorption of 5% and total shrinkage of 19%. LT2 clays from the Belyi Kolodets and Strelitsa Blizhnyaya Sections sinter at 1450°C and are characterized by 5% water absorption and 17 – 18% total shrinkage. LT3 clays from the Belyi Kolodets Section are close to caking at 1450°C. The other grades of clays do not sinter at 1450°C, forming light gray and light beige medium-strength and strong crock with 5 – 10% water absorption. The ceramic properties of the clays (firing temperature of 1250°C) are reported in Table 4.

Clays of the high grades (LOC, LT1, LT2, and LT3) are widely used in the porcelain-faience industry. The basic and semiacid grades of clays are used in fabrication of sanitary and technical articles, ceramic facing tile, in slip paste compositions, for glazes and engobe, in production of clear-fired, white, light gray, yellow, straw-colored, apricot, pink, brown, and other colors of ceramic face brick. The different clay grades are used in production of high-quality cement.

The clay is selectively mined by rotary excavators. A total of seven grades of clay produced at Voronezh Mine Management Co. has been distinguished (Table 5).

Grading warehouses have been organized at Voronezh Mine Management Co. and rigorous control of the quality of the raw material in quarries, warehouses, and customer shipments has been established.

The Shramovsk refractory clay deposit. Refractory, clear-fired clays suitable for use in production of construction ceramics have been found In the north of the Kantemirovsk and the south of the Rossoshansk regions. The useful horizon is confined to deposits of the Bereksk series of the Neogenic-Paleogenic system. Ceramic clays are common within the limits of the watersheds where they were protected from erosion at a later time. They lie horizontally. The absolute roof marks of the clays vary from 186 to 194 m over the entire area. Within the individual sections, variation of the occurrence of the clays is no greater than 2 – 3 m. The depth of the ceramic clays varies from 1.5 to 3.4 m. The blanket is composed of sands of the Bereksk series, clays, and loams of the quaternary system with a total depth of 1.5 – 24.0 m. The usable horizon is underlaid by argillaceous sands and loams of the Bereksk series and sands of the Kantemirovsk series.

Two grades of clays are distinguished within the boundaries of the productive seams: light yellow clays occur in

TABLE 5

Index	Clay						
	LOC	LT1	LT2	LT3	LTPK	LTK	LTU
Mass fraction, %:							
Al_2O_3, min	39	37	33	28	23	15	28
Fe_2O_3, max	1.5	1.5	2.0	2.5	Not standardized		3.5
Weight change in calcination, %, max	15	18	20	20	14	12	35
Refractoriness, °C, min	1730	1730	1690	1670	1670	1670	1670

TABLE 6

Clay	Mass content, %									
	SiO_2 (free)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	calcination loss
Yellow	23.33	59.14	23.58	5.26	1.53	0.61	0.36	0.37	1.75	8.29
Gray	24.00	62.40	22.24	4.30	1.39	0.70	0.36	0.38	1.93	7.88

TABLE 7

Clay	Hygroscopicity, %	Content, %, fraction, mm						Plasticity number	Refractoriness, °C
		1.0 – 0.06	0.06 – 0.05	0.05 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001		
Yellow	5.27	0.21	None	9.06	7.07	26.65	57.01	22.66	1580
Gray	4.37	0.66	″	15.06	4.03	24.14	56.11	22.20	< 1580

the upper part (depth of 0.5 – 3.5 m) and light gray clays occur in the lower part (depth of 0.4 – 1.5 m). The clays basically differ in the iron content (5.25% in yellow clays versus 4.12% in gray clays). Despite the difference in color, mining and use of the mixed clay as one grade are recommended.

Within the limits of the entire deposit, the clays are characterized by similar chemical, mineral, and disperse compositions and stable physicomechanical and process properties.

With respect to refractoriness, the clays belong to the high-melting group. The refractoriness varies from 1530 to 1580°C.

The clays are semiacid based on the alumina content. The Al_2O_3 content is 22 – 24.0% (Table 6).

The clays belong to the group with a high coloring oxide content. The mass fraction of Fe_2O_3 is 4.78% on average, 5.25% in yellow clays and 4.13% in gray clays.

The clays are characterized by a low content of water-soluble salts: 2.38 meq per 100 g of clay on average, varying from 1.62 to 3.42 meq.

With respect to the mineral composition, the clays are polymineral. Kaolinite and montomorillonite predominate (42.1 and 33.6%, respectively), and hydromica is present (13.8%).

The clays are basically medium-disperse and rarely highly disperse. The content of the less than 0.001 mm fraction is 56.1 – 57.0%, rarely attaining 60.5%. The raw material is slightly oversanded, and the total residue on a No. 063 sieve is 1.89 – 3.86%. The physicomechanical properties of the clays are reported in Table 7.

The clays basically belong to the group of raw materials with a low content of coarse inclusions (89% of the clays) and rarely with an average content (11% of the clays). The inclusions are small and medium and are represented by grains of quartz, iron hydroxides, and carbonates 0.5 – 2.5 mm in size.

The clays are average plastic. The linear air shrinkage varies from 9.80 to 13.20%. The clays are basically highly sensitive to drying and are rarely medium-sensitive.

The raw materials belong to the average-sintering-temperature group (1200 – 1250°C). The properties of the fired clays are reported in Table 8.

The clays have an average free silica content of 15.30 – 24.97%.

On the whole, the clays satisfy the requirements of GOST 9169–75 “Clay Raw Material for the Ceramics Industry” and can be used for manufacturing ceramic tiles for interior wall facing, floors, glazed and unglazed façade tiles, and for manufacturing sewage pipes. The high plasticity number of the clays (25.0 – 31.0%) is an exception and must be taken into consideration in constituting slip pastes.

The major possibility of producing ceramic face brick using clays from the Shramovsk deposit has been established. The brick brand is 125 – 250. Moreover, it is technologically difficult to use the clays in production of ceramic face brick due to the high plasticity and molding moisture content. To intensify production of ceramic face brick, Shramovsk deposit clays have to be combined with other low-plasticity clays.

The Shramovsk deposit has a favorable geographic location and is characterized by good mining conditions and large reserves. For this reason, the clays will be in wide demand by the ceramics industry.

TABLE 8

Clay	Firing temperature, °C	Shrinkage on firing, %	Water absorption, %	Color after firing
Yellow	1000	1.6	14.8	Red
	1150	7.2	5.7	–
Gray	1000	2.5	15.4	Light cream
	1150	8.6	4.3	Beige